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(54) Title: DETERGENT COMPOSITION COMPRISING CLAY FLOCCULATING POLYMER WITH PARTICLE SIZE LESS THAN 250 MICRONS

(57) Abstract

The invention relates to a granular detergent composition comprising (i) a softening clay and (ii) a clay flocculating polymer, and to a process for making the composition. The composition is particularly useful in "softening-through-the-wash" products. The clay flocculating polymer is sieved or ground such that at least 95 % by weight of the clay flocculating polymer has a particle size of less than 250 micrometers, and preferably less than 150 micrometers, before adding it to the granular detergent composition.

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DETERGENT COMPOSITION COMPRISING CLAY FLOCCULATING POLYMER WITH PARTICLE SIZE LESS THAN 250 MICRONS.

The invention relates to a granular detergent composition comprising (i) a softening clay and (ii) a clay flocculating polymer, and to a process for making the composition. The composition is particularly useful in "softening-through-the-wash" products.

Clay flocculating polymer, such as polyethylene oxide having high molecular weight, is commercially available as a 100% active powder.

EP-A-0 299 575, published on 18th January 1989, discloses granular detergent compositions comprising softening clay and polymeric clay-flocculating polymer. It is stated that in preparing a granular detergent composition the polymeric clay-flocculating agent can be added in a variety of ways. It may be added to the crutcher mix prior to spray-drying; or it may be sprayed onto a granular detergent from a solution in water or an organic solvent; or it may be dry-mixed, in the form of particles, with a granular detergent. This application does not mention preferred particle size of clay flocculating polymer.

However, when polymeric clay flocculating polymers are dry mixed to granular detergents, undesirable patchy clay deposition or residues are observed. Patchy deposition is where visible lumps of clay deposit on a fabric surface. It is caused when the clay particles are flocculated very rapidly before they have had chance to disperse. This leads to the formation of lumps of clay which deposit on the fabric surface. Residues are caused when high local concentrations of the clay flocculating polymer, present in the formulation, form gels on contact with water, leading to poor dispensing of the product and an increased risk of product deposition on clothes.

Furthermore, clay flocculating polymers when handled in particulate form, give rise to handling and explosivity problems.

Summary of the Invention

According to the present invention undesirable patchy clay deposition and residues are avoided by sieving or grinding the clay flocculating polymer such that at least

95% by weight of the clay flocculating polymer has a particle size of less than 250 micrometers, and preferably less than 150 micrometers, before adding it to the granular detergent composition.

Preferably the clay flocculating polymer is a polyethylene oxide with an average molecular weight of between 100 000 and 10 million, more preferably between 150 000 and 800 000.

In a further aspect of the invention, a process for making a granular detergent composition is provided, comprising the step of premixing the clay flocculating polymer with a powder selected from the group consisting of aluminosilicate, silicate, carbonate, citrate, phosphate, or mixtures thereof, and subsequently mixing the premix with other detergent components.

Preferably the premix consists of the clay flocculating polymer and aluminosilicate in a ratio of from 1:20 to 20:1.

Detailed Description of the Invention

Softening clay

Softening clays may be either unmodified or organically modified. Those clays which are not organically modified can be described as expandable, three-layered clays, i.e., aluminosilicates and magnesium silicates, having an ion exchange capacity of at least 50 meq/100g. of clay and preferably at least 60 meq/100 g. of clay. The starting clays for the organically modified clays can be similarly described. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites. There are two distinct classes of smectite-type clays that can be broadly differentiated on the basis of the numbers of octahedral metal-oxygen arrangements in the central layer for a given number of silicon-oxygen atoms in outer layers. A more complete description of clay minerals is given in "Clay Colloid Chemistry" by H. van Olphen, John Wiley & Sons (Interscience Publishers), New York, 1963. Chapter 6, especially pages 66-69.

The family of smectite (or montmorillonoid) clays includes the following trioctahedral minerals: talc; hectorite; saponite; sauconite; vermiculite; and the following dioctahedral minerals: prophyllite; montmorillonite; volchonskoite and nontronite.

The clays employed in these compositions contain cationic counterions such as protons, sodium ions, potassium ions, calcium ions, and lithium ions. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation :

$$\text{smectite clay } (Na)^+ + NH_4OH \Rightarrow \text{smectite clay } (NH_4)^+ + NaOH.$$

Since in the foregoing equilibrium reaction, an equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of milliequivalents per 100 g. of clay (meq/100g). The cation exchange capacity of clays can be measured in several ways, including by electrodialysis, by exchange with ammonium ion followed by titration, or by a methylene blue procedure, all as fully set forth in Grimshaw, "The Chemistry and Physics of Clays", pp. 264-265, Interscience (1971). The cation exchange capacity of a clay material relates to such factors as the expandable properties of the clay, the charge of the clay (which in turn is determined at least in part by the lattice structure), and the like. The ion exchange capacity of clays varies widely in the range form about 2 meq/100 g. of kaolinites to about 150 meq/100 g., and greater, for certain smectite clays.

Preferred smectite-type clays are sodium montmorillonite, potassium montmorillonite, sodium hectorite and potassium hectorite. The clays used herein have a particle size range of up to about 1 micron.

Any of the clays used herein may be either naturally or synthetically derived.

Clay Flocculating Polymer

Most clay flocculating polymers are fairly long chained polymers and co-polymers derived from such monomers as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone and ethylene imine. Gums, like guar gum, are suitable as well.

Preferred are polymers of ethylene oxide, acrylamide or acrylic acid. These polymers dramatically enhance the deposition of a fabric softening clay if their molecular weights are in the range of from 100 000 to 10 million. Preferred are such polymers having a weight average molecular weight of from 150000 to 5 million.

The most preferred polymer is poly (ethylene oxide). Molecular weight distributions can be readily determined using gel permeation chromatography, against standards of poly (ethylene oxide) of narrow molecular weight distributions.

Process

The particle size of the polymer is reduced by either a standard milling operation or through physical screening of the particles. The raw material is then optionally mixed with a powder, such as fine aluminosilicate (Zeolite type A) in a mixer and then added to a finished product process. The zeolite acts as a carrier for the polymer, helping to aid its dispersion in the finished product making.

Many types of particle size alteration equipment can be used to reduce the mean particle size of the clay flocculating polymer to below 250 micrometers. Continuous screens such as Russel Finex and Mogenson vibratory screens, or continuous scraper screens. Batch screening operations involving RoTap variants are also applicable for small quantities. For larger scale operations, continuous air jet mills can be used that both size reduce and classify the material at the same time.

In a particular embodiment of the invention the polymer particles may be treated by micronisation to further reduce mean particle size.

Other detergent components

The particulate components of the present invention will normally be incorporated into finished detergent products, especially those comprising softening clay. Other conventional detergent ingredients such as anionic and nonionic surfactants, builders, bleach, bleach activator, suds suppressor, enzymes (e.g. protease, amylase, cellulase, lipase), perfume brightener, soil release polymer will commonly be used.

EXAMPLES

In these examples all percentages are by weight unless otherwise specified, and the following abbreviations have been used:

PEO (as is): Polyethyleneoxide polymer as supplied by Union Carbide as WSRN750 (Trade Name). Typical particle size distribution:

2% above 710 micrometers
8% between 710 and 500 micrometers
20% between 500 and 250 micrometers
30% between 250 and 150 micrometers
40% below 150 micrometers

PEO (sized): As above but with 95% of the material above 150 micrometers removed via a size reduction process. Typical particle size distribution:

At least 100% below 300 micrometers
At least 95% below 150 micrometers
At least 50% below 106 micrometers

Zeolite A : supplied by Industrial Zeolite Ltd., Thurrock, England. Typical mean particle size: 2-10 micrometers.

Light Soda Ash A: light density sodium carbonate, typically 97% pure carbonate, a mean particle size of approx 100 micrometers, and an aerated density averaging 550 g/l.

Example 1

A sample of PEO (as is) was converted to PEO (sized) by the procedure of RoTap batch screening on a 150 micrometer sieve. The resulting polymer was mixed to a homogeneous state in a small scale food processor with the ratio: 1 part PEO (sized) to 2 parts Zeolite A.

The PEO/Zeolite A premix was mixed in a batch rotary mixer together with the particulate components of a "softening through the wash" detergent composition shown below. Liquid components were then sprayed on. The finished composition has excellent clay deposition and softening properties.

	Example 1 (% by weight)
PEO / Zeolite A premix	0.5
Softening clay	18
Anionic Surfactant Agglomerate	26
Cationic Surfactant Agglomerate	6
Nonionic Surfactant	3
Sodium Percarbonate	13
Layered Silicate / Citric Acid	12
Zeolite	4
Bleach Activator Particle	4
Suds Suppressor	3.5
Sodium Carbonate, Enzymes, Perfume, Soil Release Polymer, Brightener and other minors	balance to 100

Example 2

Example 1 was repeated, except that the size reduction step was completed by passing PEO (as is) through a continuous Russel Finex vibratory screening system loaded with a 150 micrometer sieve.

Example 3

Example 1 was repeated, except the size reduction procedure involves milling the PEO (as is) in a small batch coffee grinder and then completing the RoTap batch screening. This eliminates any PEO (as is) wastage.

Example 4

Example 1 was repeated except size reduction procedure was carried out by passing PEO (as is) through a standard non-vibrating sieve deck loaded with a 150 micrometer screen and fitted with rotary brushes to improve screening efficiency.

Example 5

Example 1 was repeated, except size reduction procedure was carried out by passing PEO (as is) through a standard Air Jet Mill operating such that only particles below 150 micrometers are entrained in the air flow and removed for collection. This procedure eliminates wastage of PEO (as is) and is useful for large scale volume requirements.

Example 6

Example 4 was repeated, except the PEO (sized) was mixed with Zeolite A in a batch vertomixer, or similar equipment, incorporating a conical mixer with a screw rotating on its own axis which at the same time orbits the mixing chamber.

Example 7

Example 6 was repeated, except the resultant premix contains a ratio of 1 part PEO (sized) to 1 part Zeolite A.

Example 8

Example 6 was repeated, except the resultant premix contains a ratio of 1 part PEO (sized) to 10 parts Zeolite A.

Example 9

Example 8 was repeated, except that the resultant premix contains a ratio of 1 part PEO (sized) to 10 parts fine light soda ash.

Example 10

Example 6 was repeated except that the premix was added directly to a continuous detergent production process before any liquid spray ons.

Example 11

Example 6 was repeated, except that the premix was dusted onto the surface of a detergent produced on a continuous production process, after any liquid spray ons.

What is claimed is:

1. A granular detergent composition comprising (i) a softening clay and (ii) a clay flocculating polymer characterised in that at least 95% by weight of the clay flocculating polymer has a particle size of less than 250 micrometers.

2. A granular detergent composition according to claim 1 wherein at least 95% by weight of the clay flocculating polymer has a particle size of less than 150 micrometers.

3. A granular detergent composition according to either claim 1 or claim 2 wherein the clay flocculating polymer is a polyethylene oxide with an average molecular weight of between 100 000 and 10 million.

4. A granular detergent composition according to claim 3 wherein the clay flocculating polymer is a polyethylene oxide with an average molecular weight of between 150 000 and 800 000.

5. A process for making a granular detergent composition according to any of the previous claims, further comprising a powder selected from the group consisting of aluminosilicate, silicate, carbonate, citrate, phosphate, or mixtures thereof, and comprising the step of premixing the clay flocculating polymer with the powder to form a premix, and subsequently mixing the premix with other detergent components.

6. A process according to claim 5 wherein the premix consists of the clay flocculating polymer and aluminosilicate in a ratio of from 1:20 to 20:1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/14106

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C11D 3/12, 3/37, 7/20, 9/18, 17/06.
US CL :510/308, 322, 334, 360, 475, 506, 507.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/308, 322, 334, 360, 475, 506, 507.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, DIALOG
search terms: polyethyleneoxide?, poly, ethylene, polyethylene, oxide?, flocculat?, clay?, bentonite?, deterg?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,443,750 A (CONVENTS ET AL.) 22 August 1995 (22/08/95), see col. 3, ll. 30-31; col. 13, l. 65 - col. 15, l. 16, especially col. 1,4 l. 66 - col. 15, l. 4; col. 16, ll. 36-41; Table V, Examples III, IV, VI-VIII (noting col. 22, ll. 19-20, 25-27).	1-4
A	US 4,844,821 A (MERMELSTEIN ET AL.) 04 July 1989 (04/07/89), see Examples 2 & 7 in cols. 21-22.	1-4

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search 13 OCTOBER 1996	Date of mailing of the international search report 17 JAN 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer Nabendra Roy GARDITH HERTZOG Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)★

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/14106

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect f certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5 & 6
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.